Observation of semilocalized dispersive states in the strongly correlated electron-doped ferromagnet Eu\(_{1-x}\)Gd\(_x\)O


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Observation of semi-localized dispersive states in the strongly correlated electron-doped ferromagnet $\text{Eu}_{1-x}\text{Gd}_x\text{O}$

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Chemical substitution plays a key role in controlling the electronic and magnetic properties of complex materials. For instance, in EuO, carrier doping can induce a spin-polarized metallic state, colossal magnetoresistance, and significantly enhance the Curie temperature. Here, we employ a combination of molecular-beam epitaxy, angle-resolved photoemission spectroscopy, and an effective model calculation to investigate and understand how semi-localized states evolve in lightly electron doped $\text{Eu}_{1-x}\text{Gd}_x\text{O}$ above the ferromagnetic Curie temperature. Our studies reveal a characteristic length scale for the spatial extent of the donor wavefunctions which remains constant as a function of doping, consistent with recent tunneling studies of doped EuO. Our work sheds light on the nature of the semiconductor-to-metal transition in $\text{Eu}_{1-x}\text{Gd}_x\text{O}$ and should be generally applicable for doped complex oxides.

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Chemical substitution is one of the most common pathways for controlling the electronic properties of semiconductor materials, from modifying the resistivity of semiconductors, realizing high-temperature superconductivity, or accessing nanoscale spin, charge, or orbitally ordered states. When stoichiometric, the binary oxide EuO is a dense ferromagnet ($S = 7/2$) with a half-filled, $4f^7$ shell. Carrier doping induces a number of remarkable properties, including a metal-insulator transition ($\Delta \rho/\rho_0 \approx 10^{13}$), colossal magnetoresistance ($\Delta \rho/\rho_0 \approx 10^8$), an enhancement of the Curie temperature ($T_C$), and highly spin-polarized carriers (> 90%), leading many to explore this material for спинtronic applications e.g., a spin valve. Carrier doping can be achieved in EuO by a number of methods, including oxygen vacancies or the substitution of Eu with Gd, leading to the introduction of $n$-type donors which ultimately results in a degenerately doped phase at high doping. Nonetheless, how the electronic structure of this system evolves in the low doping regime remains an open question.

In a simple band-insulator scenario, one might expect metallic behavior from doping even an infinitesimal amount of carriers, although in reality, an insulating ground state persists for some finite range of doping. Metallic behavior is not achieved until enough donors are introduced such that their wave functions begin to overlap to the point where they form a degenerate state. In typical Group IV doped semiconductors such as Si:P, the Bohr radius of the donors can be many tens of angstroms, meaning that this semiconductor-to-metal transition occurs at very low carrier concentrations of $n \approx 10^{18}$ cm$^{-3}$. The low concentration makes it difficult to probe this regime using direct probes of the electronic structure such as angle-resolved photoemission spectroscopy (ARPES), since the photoemission intensity is proportional to the total number of states. Furthermore, it remains unclear whether this phenomenology from conventional semiconductors can also be applied to strongly correlated magnetic materials such as $\text{Eu}_{1-x}\text{Gd}_x\text{O}$. In many oxides including EuO, this transition occurs at significantly higher densities, typically on the order of $n \approx 10^{20}$ cm$^{-3}$, making this regime accessible by ARPES and related techniques. Despite the strong Coulomb interactions, which split the $4f$ states, above $T_C$ one can approximate EuO as a semiconductor with a band gap ($\sim 1.1$ eV) separating an occupied Eu $4f$ valence band from an unoccupied Eu 5d conduction band.

Here, we report the evolution of the electronic structure at low carrier dopings in electron-doped $\text{Eu}_{1-x}\text{Gd}_x\text{O}$, using a combination of reactive oxide molecular beam epitaxy, ARPES, and model Hamiltonian calculations to explain our observations. Thin films of (001) $\text{Eu}_{1-x}\text{Gd}_x\text{O}$ were grown on (110) YAlO$_3$ single crystal substrates by molecular beam epitaxy in both a dual chamber Veeco 930 and GEN10 system. The substrate was heated to 400 °C during growth, resulting in adsorption-controlled growth of EuO, which minimizes oxygen nonstoichiometry. The Eu flux was 1.1 $\times 10^{14}$ atoms/cm$^2$s, and the Gd flux was varied to achieve different doping levels ($x$). Film quality was monitored during
growth using reflection high-energy electron diffraction. Following growth, the films were immediately transferred to the ARPES system without breaking ultra-high vacuum ($2 \times 10^{-10}$ torr). ARPES measurements were performed using a VG Scienta R4000 spectrometer and He Ia photons ($h\nu = 21.2$ eV) The instrumental energy resolution was $\Delta E = 25$ meV and the base pressure typically was better than $6 \times 10^{-11}$ torr.

We begin our discussion by analyzing the doping-dependent ARPES spectra for Eu$_{1-x}$Gd$_x$O ($x = 0.013$, 0.05, and 0.21) at a fixed temperature, $T = 140$ K, above $T_C$ for all samples. Prior work$^{11}$ has revealed that above $T_C$, carriers introduced by rare earth doping result in the formation of a circular electron pocket near the Brillouin Zone center $\Gamma$ ($k_x, k_y$) = 0, shown in Fig. 1(a, inset). At the lowest doping levels ($x = 0.013$, which sits on the boundary of the insulator-to-metal transition), the spectral weight near $E_F$ is comprised of a nearly featureless patch of intensity; samples with doping levels below $x = 0.013$ showed no observable weight near $E_F$ and charged up electrostatically above $T_C$ during measurements, suggesting these states are bulk-derived and do not arise from surface states or surface accumulation layers. Upon moving to higher doping levels, the spectral features evolve to a dispersive band which can be clearly observed for $x = 0.21$, well in the metallic regime. The evolution of $k_F$ with $x$ [Fig. 1(d)] shows that the size of this pocket increases with Gd content, consistent also with higher carrier densities observed by Hall effect measurements at 4.2 K.$^{14}$

While our ARPES measurements characterize how these doping-induced states evolve with $x$, the nature and origin of these states is unclear. As noted in Ref. 11, a rigid band shift alone cannot explain the appearance of a pocket around the $\Gamma$ point, as the conduction band minimum should be at the Brillouin zone boundary ($X$ point). Major advances have been made in calculating the effects of disorder on the band structure in the iron-based superconductors and other systems by employing a combination of supercell band structure calculations coupled with an unfolding procedure.$^{15,16}$ Due to the correlated nature of EuO and the relatively low doping limit that we are investigating, we instead employ a qualitative model Hamiltonian considering dilute impurity states$^{17}$ that weakly overlap. In the following, we describe the impurity states by means of a tight-binding model,

$$\mathcal{H} = \sum_{i\neq j} t_{ij} d_i^\dagger d_j + \sum_i \epsilon_i d_i^\dagger d_i \equiv \sum_{i,j} \mathcal{H}_{ij} d_i^\dagger d_j,$$

(1)

where the sums run over the $n = xN$ (random) impurity sites with random on-site potential $\epsilon_i$ and $t_{ij}$ are the hopping integrals. Note that the operator $d_i^\dagger$ creates an electron at the impurity site $i$ in a spatially-extended impurity-state wavefunction $\phi_i(i\vec{r} - \vec{r}_i)$. Using the Fourier transform $\tilde{\phi}_i(\vec{k})$ of these wave functions, we can thus express the electron Green’s function in terms of the tight-binding propagator $g(i, j, \omega) = [(\omega - \mathcal{H})^{-1}]_{ij}$,

$$G^{(ret)}(\vec{k}, \vec{k'}, \omega) = \sum_{i,j} \tilde{\phi}_i(\vec{k}) \tilde{\phi}_j(\vec{k'}) e^{i(\vec{r}_i - \vec{r}_j)} g(i, j, \omega^+) \quad (2)$$

Finally, the single-electron spectral density measured by ARPES can be calculated as

$$A(\vec{k}, \omega) = -\frac{1}{\pi} \text{Im} G^{(ret)}(\vec{k}, \vec{k}, \omega). \quad (3)$$

For the case of localized impurities, i.e., $t_{ij} \equiv 0$, the spectral function is the sum of the individual impurity spectral functions, $S_i(\vec{k}, \omega) = |\phi_i(\vec{k})|^2 \delta(\omega - \epsilon_i)$, such that
the width of the ARPES signal in momentum space is
given by the inverse of the size of the impurity state in
real space. For the semi-localized case, where the im-
purity states with the Gaussian envelope removed to high-
light the impurity band dispersion. (b-d) Isolated impurity
band spectral functions calculated for doping values of 1/8,
1/4, and 1/2. The range of the color scales for each panel in
has been individually normalized to make the impurity bands
more visible.

the width of the ARPES signal in momentum space is
given by the inverse of the size of the impurity state in
real space. For the semi-localized case, where the im-
purity wave functions overlap, we can approximate the
spectral function by

\[ S(\vec{k}, \omega) \approx |\tilde{\phi}(\vec{k})|^2 \left( -\frac{1}{\pi} \text{Im} \left( \sum_{i,j} e^{i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} g(i, j, \omega^+) \right) \right) \]  

(4)

assuming that all of the impurity wave functions are
approximately the same. The electron Green’s function is
thus given by the Fourier transform of the tight-binding
propagator, with $|\tilde{\phi}(\vec{k})|^2$ as an envelope function.

Figure 2 exemplifies the resulting effect on the single-
electron spectral density by using a one-dimensional
model. Note that for simplicity, we use Gaussian im-
purity wave functions with a width $r_0$. A key result from
this model calculation is that the envelope of the spectral
intensity observed in ARPES for the doped carriers is set
by the Fourier transform of this Gaussian envelope and
is doping independent. In addition, we allow for an ex-
tended hopping of the form $t_{ij} = t \exp(-t_{ij}^2/2r_0^2)$,
with the hopping energy $t$ setting the energy scale. This
hopping accounts for the extended nature of the impuri-
ty states and leads to an appreciable dispersion around
the $\Gamma$ point, even at low doping, consistent with the lo-
cation in momentum space of the semi-localized states
observed in experiment in Fig. 1. The spectral functions
are averaged over 100 random impurity arrangements,random on-site energies $\epsilon_i/t \in [-0.5 - 0.05, -0.5 + 0.05]$ and $r_0 = 4a$ shown both with and without this envelope, and with the envelope at three different doping values. Our calculation illustrates the formation of a dispersive impurity band, together with the momentum-dependent suppression of intensity when moving away from $\Gamma$, which is parameterized by the spatial extent of the impurity state, $r_g$.

Having established a simple model which accounts
qualitatively for the features of our ARPES data, we
now proceed with a more quantitative analysis of our
experimental data. Prior ARPES data\textsuperscript{11} has revealed
two species of charge carriers coexisting around $\Gamma$, which
can be described as 1) electrically active carriers which
participate in the temperature dependent metal-insulator
transition [green in Fig. 3(a)], and 2) electrically inac-
active or deeply bound electrons which remain trapped at
all temperatures [blue in Fig. 3(a)]. The ratio between
these two different states is also approximately consistent
with the ratio of the free carriers deduced by Hall mea-
surements versus the percentage of doped Gd cations, on
the order of 50%.\textsuperscript{11} Nonetheless, an exact equality
between the Gd concentration and $k_F$ cannot be directly
established, due to uncertainties in the three-dimensional
electronic structure in the $k_z$ direction. We note that the
model Hamiltonian only considers the electrically active
species of charge carrier. Therefore, to isolate the rel-

vant electrically active carriers from the deeply bound
states (which are not considered in this work), we
subtract the integrated spectral weight at low temperatures
around $\Gamma$ from the data measured at 140 K, the results
of which are shown in Figs. 3(b-d). We follow this pro-
cedure because below $T_C$, the mobile carriers are trans-
ferred to the $X$ point (the majority spin conduction band
minimum), while the deeply bound states are present at
all temperatures; therefore, the difference in intensity
above and below $T_C$ should represent solely the mobile
carrier contribution above $T_C$.

In Fig. 3(e), we plot the subtracted MDCs (green) for
all three doping values on the same axes, each normal-
ized to their maximum intensity. While there are subtle
intensity variations at larger $k$, it is rather striking that
the full width at half maximum (FWHM) of each curve
is essentially identical (0.39 ± 0.03 Å\textsuperscript{−1}), despite an
expected significant overlap of the impurity wave functions
and having $k_F$‘s which differ by as much as a factor of 2 [Fig.
1(d)]. This result is strongly suggestive that there is a momentums-dependent suppression of the spec-
tral function, as predicted by our model Hamiltonian in
Eq. (4). The uniform momentum-space width described
above corresponds to a value of $r_0 = 4.3$ Å and a real
space FWHM of $\Delta r = 10$ Å, which is remarkably close
to the value for $a_B = 12$ Å, predicted using simple Thomas-
Fermi screening, where $a_B n_c^{1/3} \geq \frac{1}{3}$ and $n_c \sim 1 \times 10^{19}$
cm\textsuperscript{−3} for EuO. Given the fcc EuO lattice with 12-fold
coordination and an Eu-Eu nearest neighbor distance of
3.6 Å, the donor extends over multiple lattice sites, con-
sistent with our envelope of intensity in $k$-space. These

FIG. 2. (a) Simulated spectral function for a one-dimensional
system ($N = 1000$ sites) consisting only of spatially extended
impurity states with the Gaussian envelope removed to high-
light the impurity band dispersion. (b-d) Isolated impurity
band spectral functions calculated for doping values of 1/8,
1/4, and 1/2. The range of the color scales for each panel in
has been individually normalized to make the impurity bands
more visible.
observations are also consistent with recent atomically resolved scanning tunneling microscopy (STM) measurements on EuO$_{1-x}$ thin films by Klinkhammer et al.\textsuperscript{19}, who showed an oxygen vacancy was found to have a real space extent with FWHM $\sim 7.5$ Å. Considering that STM measures the square modulus of a real space wave function, $|\psi(x)|^2$, this would imply a wave function parameterized by $\Delta r \approx 11$ Å, in excellent agreement with our $k$-space measurements.

While our measurements indicate that the doped carriers form semi-localized states, they do not elucidate the mechanism of this localization. In conventional semiconductors, electrons are localized by the impurity-site potential in a dielectric background. Within the effective mass approximation, this results in a localization length given by the crystal Bohr radius, $a_B = \kappa_0 \hbar^2/\mu^* e^2$. While this description is not formally valid in the present case, a rough estimate can still be obtained. The static dielectric constant of undoped EuO at room temperature is $\kappa_0 = 23.9,^{20}$ while the effective mass of EuO has been previously estimated by numerous groups with results ranging from $\mu^* = 0.35 - 1.1 \mu_e.^{21,23}$ Using these values, we calculate $a_B \approx 10 - 40$ Å, comparable to our previous estimates. The correlated nature of EuO and the localized $f$ moments could also result in a different source of localization. For example, much attention has been devoted to the idea of magnetically induced localization (i.e. magnetic polarons) forming at high temperatures,\textsuperscript{24,25} where the electron is localized owing to its coupling to a disordered magnetic background, although the accuracy of this picture has been questioned recently by Monteiro et al.\textsuperscript{26}.

Recently, localized impurity states were also observed for the case of the wide-gap semiconductor Si-doped $\beta$-Ga$_2$O$_3$ in both STM\textsuperscript{27} and ARPES\textsuperscript{28}. Similarly, a consistent picture of momentum space and real space was obtained. Nonetheless, the states observed showed no sign of dispersion in ARPES. Moreover, the localized states appeared below the expected band minimum, consistent with the effective mass description, while in EuO, the localized states appear around the $\Gamma$ point, with the (conduction) band minimum located at the Brillouin-zone boundary.

In conclusion, we have investigated the semiconductor-to-metal transition in Eu$_{1-x}$Gd$_x$O through the evolution of the electronic spectral weight obtained by ARPES, finding a dispersing pocket around the $\Gamma$ point which grows with increasing electron doping $x$. Comparing to an effective model describing dilute, quasi-localized impurity states allows us to not only gain momentum-resolved spectral information from ARPES measurements on doped EuO, but also to extract the length scale related to the semiconductor-to-metal transition in this material, demonstrating the validity of this simple model even in strongly correlated materials. This length scale of $\Delta r = 10$ Å does not change with increasing doping, providing a clear signature of the Bohr radius of the previously localized impurity states, even well into the metallic regime.

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